GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 12/15/80

Project Title: Further Experimental Study of Chemical Processes of Liquid Extraction

Project No: E-19-627

Project Director: Dr. A. H. P. Skelland

Sponsor: National Science Foundation; Washington, D. C. 20550

Agreement Period: From 10/15/80 Until 3/31/82
(includes usual 6 month unfunded flexibility period)

Type Agreement: Grant No. CPE-8019617

Amount:

$21,130	NSF
730	GIT (E-19-351)
$21,860	TOTAL

Reports Required: Annual Progress Report; Final Project Report

Sponsor Contact Person (s):

Technical Matters

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202/357-9606

Contractual Matters
(thru OCA)

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Section I
AAEO/EAS Branch
Division of Grants and Contracts
Directorate for Administration
National Science Foundation
Washington, D. C. 20550
202/357-9626

Defense Priority Rating: None

Assigned to: Chemical Engineering (School/Laboratory)

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 2/14/83

Project Title: Further Experimental Studies of the Chemical Process of Liquid Extraction

Project No: E-19-627

Project Director: Dr. Anthony H. Skelland

Sponsor: National Science Foundation

Effective Termination Date: 3/31/82

Clearance of Accounting Charges: 3/31/82

Grant/Contract Closeout Actions Remaining:

- [ ] Final Invoice and Closing Documents
- [x] Final Fiscal Report FCTR (SF272)
- [x] Final Report of Inventions (If positive)
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

NOTE: Final Technical Report

Submitted 2/8/83

Assigned to: Chemical Eng. (School/~~Laboratory~~)

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FINAL PROJECT REPORT
NSF FORM 98A

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PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology School of Chemical Engineering Atlanta, GA 30332	Mass Thermodynamics & Transfer	CPE-8019617
	4. Award Period From 10/15/80 To 3/31/82	5. Cumulative Award Amount $21,130

6. Project Title
Further Experimental Studies of the Chemical Process of Liquid Extraction

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

One of the biggest problems in relating correlations established in the laboratory for pure systems to industrial extraction design and operation is the interference on the industrial scale from trace amounts of unknown surface active impurities. This study forms part of a program to obtain guidance on these problems regarding specific aspects of the liquid-liquid extraction process. It was found that:

a) The Scheele and Meister correlation for predicting drop size at an immersed nozzle using pure systems is adequate for systems contaminated with surfactant, provided that the diminished value of interfacial tension is used in the computation.

b) Similar comments apply to the Klee and Treybal correlation for predicting the terminal velocities of freely falling drops.

c) The influence of surfactants on the onset of droplet oscillation has been established.

It may be noted that the Project completion date is February, 1983, since Mr. Ramsay's essential contribution was made after the grant's expiration.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses					
b. Publication Citations					
c. Data on Scientific Collaborators		✓			
d. Information on Inventions					
e. Technical Description of Project and Results					
f. Other *(specify)* First draft of manuscript for publication.		✓			

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
A.H.P. Skelland		Feb 8 '83

Part III, 1 c.

Scientific Collaborators in this project were graduate students Mrs. Sally Woo and Mr. George G. Ramsay.

EFFECTS OF SURFACE ACTIVE AGENTS ON DROP SIZE, TERMINAL VELOCITY, AND DROPLET OSCILLATION IN LIQUID-LIQUID SYSTEMS

by

A.H.P. Skelland, Sally Woo and George G. Ramsay

Chemical Engineering Department

Georgia Institute of Technology

ABSTRACT

Drop size, terminal velocity, and the onset of oscillation of organic drops falling through water were determined in systems containing anionic, cationic, or nonionic surfactants. Surfactant concentration, nozzle diameter, and nozzle velocity were varied to cover the range of most industrial applications of drop formation from circular orificies in the nonjetting region.

Existing correlations for drop size and terminal velocity in uncontaminated systems are shown to be adequate in the presence of surfactants when used with the diminished value of interfacial tension. The applicability of criteria for the onset of oscillation in pure systems to those containing surfactants is examined.

INTRODUCTION

Much effort has been spent studying drops in liquid-liquid systems. Most of this work, however, has been done with "pure" or "nearly pure" components, whereas actual applications often contain significant contamination and this results in uncertainty about applying laboratory correlations to industrial systems. The purpose of this paper is to develop some "rules of thumb" about the effectiveness of some of these correlations in the presence of surfactants (SAA).

Because the area available for mass transfer is so important, the sizes of drops formed in the presence of surfactants were compared with those predicted by Scheele and Meister's (1968) correlation for uncontaminated systems.

It has long been known that surfactants decrease terminal velocity (and mass transfer) by inhibiting internal circulation (Garner and Skelland, 1955). The present study attempts to quantify this effect by comparing the terminal velocity of contaminated drops with predictions from Klee and Treybal's (1956) equations.

Schroeder and Kintner (1965) showed that drop oscillation greatly increases the rate of heat and mass transfer. Criteria for the onset of oscillation are given by Hu and Kintner, 1955; Klee and Treybal, 1956; Johnson and Braida, 1957; Edge and Grant, 1971; and Grace et al, 1976. The applicability of these criteria in the presence of surfactants is investigated.

EXPERIMENTAL

The experimental apparatus included a constant head 50 ml buret, fitted with various sizes of glass nozzle via a ground glass joint. The tip of the nozzle was submerged in a solution of water and surfactant, and chlorobenzene was placed in the buret and allowed to form drops at the inner edge of the nozzle tip. A constant flowrate was maintained by placing a narrow glass tube down most of the length of the buret and forming a tight seal at the top with a rubber stopper (see for example Skelland and Wellek, 1964).

Eleven nozzles were used with internal diameters ranging from 0.0064 cm to 0.5527 cm. The anionic surfactant was dodecyl sodium sulfate, the cationic surfactant was dodecyl pyridinium chloride, and the nonionic surfactant was phenoxy polyethoxyethanol; all were dissolved in the aqueous phase. Figure 1 shows the effects of concentration of surfactant on interfacial tension, as measured by Harkins and Brown's (1919) drop weight method. Onset of droplet oscillation was determined both visually and by the location of the maxima in the plots of u_t vs. d_p in Figures 4a and 4b.

DISCUSSION

Drop volumes were predicted by using the diminished value of interfacial tension (due to the presence of surfactant) in Scheele and Meister's equation, given below.

$$V_p = F \left\{ \frac{\pi \sigma g_c d_o}{g \Delta \rho} + \frac{5 \pi \mu_c d_o^3 u_o}{d_p^2 g \Delta \rho} - \frac{\pi \rho_d d_o^2 u_o^2}{4 g \Delta \rho} + 4.5 \left[\left(\frac{\pi d_o^3 u_o}{4 g \Delta \rho} \right)^2 \rho_d \sigma g_c \right]^{\frac{1}{3}} \right\} \qquad (1)$$

Runs for the pure system showed good agreement with equation (1) except when d_o was below the range used by Scheele and Meister (0.0813 cm to 0.688 cm). For d_o less than about 0.06 cm equation (1) showed an increasing tendency to

underpredict as d_o became smaller and even gave a negative value for V_p when d_o was 0.0064 cm. Also the only two runs with d_o of 0.0137 cm, which used the anionic surfactant, gave negative predicted drop volumes. In order to make an accurate evaluation of equation (1), data outside the range used by Scheele and Meister were not included in the analysis.

Because the interfacial tension at the edge of the nozzle during rapid drop formation is probably higher than that measured at equilibrium, it may be anticipated that predictions of such drop volumes from equation (1) using equilibrium values of σ would be lower than the measued values.

The mean deviation, defined as $\sum (V_{cal} - V_{exp})/nV_{exp}$ and the mean absolute deviation, defined as $\sum |V_{cal} - V_{exp}|/nV_{exp}$, were used to evaluate the data. Analysis of Scheele and Meister's original data showed a mean deviation of 6.3%, which indicates a tendency to overpredict, whereas the 219 runs in the presence of surfactants had a mean deviation of -5.0%, indicating a tendency to underpredict. Fortunately, the two trends tend to cancel each other and this is illustrated by the fact that the original authors had a mean absolute deviation of 11.0% whereas the mean absolute deviation in the presence of surfactants was 11.5%. These results are shown in Figure 2.

Analysis of variance indicated that the type of surfactant has little effect on the calculation of drop volume from equation (2).

The criterion for critical drop diameter for the beginning of droplet oscillation developed by Klee and Treybal (1956) is

$$d_{pc} = 0.33 \rho_c^{0.14} \Delta\rho^{-0.43} \mu_c^{0.30} \sigma^{0.24} \qquad (2)$$

and the terminal velocity u_t is given by

$$u_t = 38.3 \rho_c^{-0.45} \Delta\rho^{0.5} \mu_c^{-0.11} d_p^{0.70} \qquad (3)$$

For $d_p < d_{pc}$

$$u_t = 17.6 \rho_c^{-0.55} \Delta\rho^{0.73} \mu_c^{0.13} \sigma^{0.13} \qquad (4)$$

for $d_p > d_{pc}$

The diminished values of interfacial tension due to the presence of surfactants were used where applicable in comparing these equations with our measurements.

For equation (3) the mean absolute deviation in the presence of surfactants was 5.43%, whereas the mean absolute deviation for Klee and Treybal's data was 4.15%. Our 34 runs for this equation were not sufficient to draw any conclusions about the effect of different surfactants.

For equation (4) the mean absolute deviation in the presence of surfactants was 4.45% for the 191 runs, whereas the mean absolute deviation for Klee and Treybal's data was 2.82%. Analysis of variance indicated that the type of surfactant had no effect on the calculation of u_t with equation (4).

The mean deviations for equations (3) and (4) were -4.13% and -3.05%, respectively. This shows a slight additional reduction in terminal velocity beyond the accomodation provided by use of the diminished interfacial tension values due to SAA in equations (3) and (4). The results are shown in Figure 3.

Next, the onset of oscillations in the presence of surfactants will be compared with several established criteria for pure systems. Figures 4a and 4b show that u_t is at or near a maximum when d_p equals d_{pc}, whether surfactants are present or not.

Hu and Kintner (1955) proposed that oscillations begin when

$$N_{We} > 3.58 \qquad (5)$$

As shown in Figure 5, the N_{We} at which oscillation starts increases as the concentration of surfactant increases and then passes through a maximum. For equation (5) the mean deviation was -23.4% and the mean absolute deviation was 25.9%.

Klee and Treybal's criterion for the onset of oscillation is equation (2) and experimental results are shown in Figure 6. For the pure system equation (2) underpredicts the critical drop

diameter. As the concentration of surfactant increases, the discrepancy between predicted and experimental values stays about the same for the nonionic, but decreases for the anionic and cationic surfactants. For equation (2) the mean deviation was -36.8% and the mean absolute deviation was 37.3%.

Johnson and Braida (1957) proposed that oscillation starts when

$$N_{Re} / N_P^{0.15} > 20 \qquad (6)$$

The results, shown in Figure 7, are similar to those obtained from Klee and Treybal's criterion, except that at high concentrations of anionic and cationic surfactant equation (6) overpredicts the critical drop diameter. For equation (6) the mean deviation was -10.9% and the mean absolute deviation was 16.0%.

Edge and Grant (1971) proposed

$$d_{pc} = 0.162(\rho_d / \Delta\rho)^{0.5} \qquad (7)$$

This is the only criterion for critical drop diameter that does not contain interfacial tension. Therefore, for all concentrations of surfactants, this equation predicted a critical drop diameter of 0.518 cm. Although the range of error is fairly large, equation (7) seems to lie near the middle of that range, as shown in Figure 6 and by its mean deviation of -0.6% and mean

absolute deviation of 23.2%.

Grace, Wairegi, and Nguyen (1976) established the criterion for onset of oscillation as

$$H > 59.3 \tag{8}$$

$$H = \frac{4}{3} N_{Eo} N_M^{-0.149} (\mu_c/\mu_w)^{-0.14}$$

The results of using equation (8) are illustrated in Figure 8.

This correlation is actually very similar to that of Klee and Treybal as shown by its dimensional form

$$d_{pc} = 0.36 \rho_c^{-0.15} \Delta\rho^{-0.42} \mu_c^{0.30} \sigma^{0.28} (\mu_c/\mu_w)^{0.07} \tag{9}$$

but gives better results than that of Klee and Treybal, as indicated by its mean deviation of -16.3% and mean absolute deviation of 20.2%.

CONCLUSIONS

Using the diminished value of interfacial tension due to the presence of surfactants in Scheele and Meister's equation for drop size gives results comparable to that of pure systems. The effect of type of surfactant on drop volume is small if any.

Klee and Treybal's equations for determining terminal velocity seem to be roughly adequate when the dimished value of interfacial tension due to the presence of surfactants is used. The type of surfactant seems to have no effect on terminal velocity.

Figures 4a and 4b show that u_t is at or near a maximum when d_p equals d_{pc}, whether surfactants are present or not. The effect of type of surfactant on the onset of droplet oscillation is small if any. Generally, as the concentration of surfactant increased, the actual d_{pc} decreased faster than the predicted d_{pc}.

Johnson and Braida's criterion for the onset of oscillation gave the least error but includes u_t, which may have to be estimated in practice. Grace, Wairegi, and Nguyen's criterion seems to be the best, which is probably the result of the large amount of data upon which it is based.

NOTATION

C	concentration of surfactant, g/l
d_o , d_p , d_{pc}	diameters of orifice, droplet, and droplet at onset of ocillation, cm
F	Harkins and Brown's correction factor
g, g_c	gravitational acceleration, cm/s^2 , gravitational constant
n	number of runs, unitless
N_{Eo}	Eotvos number, $gd_p^2 \Delta\rho / \sigma$
N_M	Morton number, $g \mu_c^4 \Delta\rho / \rho_c^2 \sigma^3$
N_P	$\sigma^3 \rho_c^2 / g \mu_c^4 \Delta\rho$
N_{Re}	Reynolds nymber, $d_p \rho_c u_t / \mu_c$
N_{We}	Weber number, $d_p u_t^2 \rho_c / \sigma$
u_o , u_t	velocity of fluid through orifice, terminal velocity, cm/s
V_p , V_{exp} , V_{cal}	volume of droplet, experimental value, value from Scheele and Meister equation, cm^3
μ_c , μ_w	viscosity of continuous phase and of water, poise
ρ_d , ρ_c , $\Delta\rho$	density of dispersed phase, continuous phase, and the difference between the two, g/cm^3
σ	interfacial tension, dyne/cm

LITERATURE

Edge, R.M., and Grant, C.D., Chem. Eng. Sci., 25, 1001-1012 (1971).

Garner, F. H., and Skelland, A.H.P., Chem. Eng. Sci., 4, 149 (1955).

Grace, J.R., Wairegi, T., and Nguyen, T.H., Trans. Inst. Chem. Eng., 54, 167-173 (1976).

Harkins, W.D. and Brown, F.E., J. Am. Chem. Soc., 41, 499 (1919).

Hu, S., and Kintner, R.C., A.I.Ch.E.J., 1, 42 (1955).

Johnson, A.I., and Braida, L., Can. J. Chem. Eng., 35, 165 (1957).

Klee, A.J., and Treybal, R.E., A.I.Ch.E.J., 2, 444 (1956).

Scheele, G.F., and Meister, B.J., A.I.Ch.E.J., 14, 9-19 (1968).

Schroeder, R.R., and Kintner, R.C., A.I.Ch.E.J., 11, 5-8 (1965).

Skelland, A.H.P., Wellek, R.M., A.I.Ch.E.J., 10, 491-6 (1964).

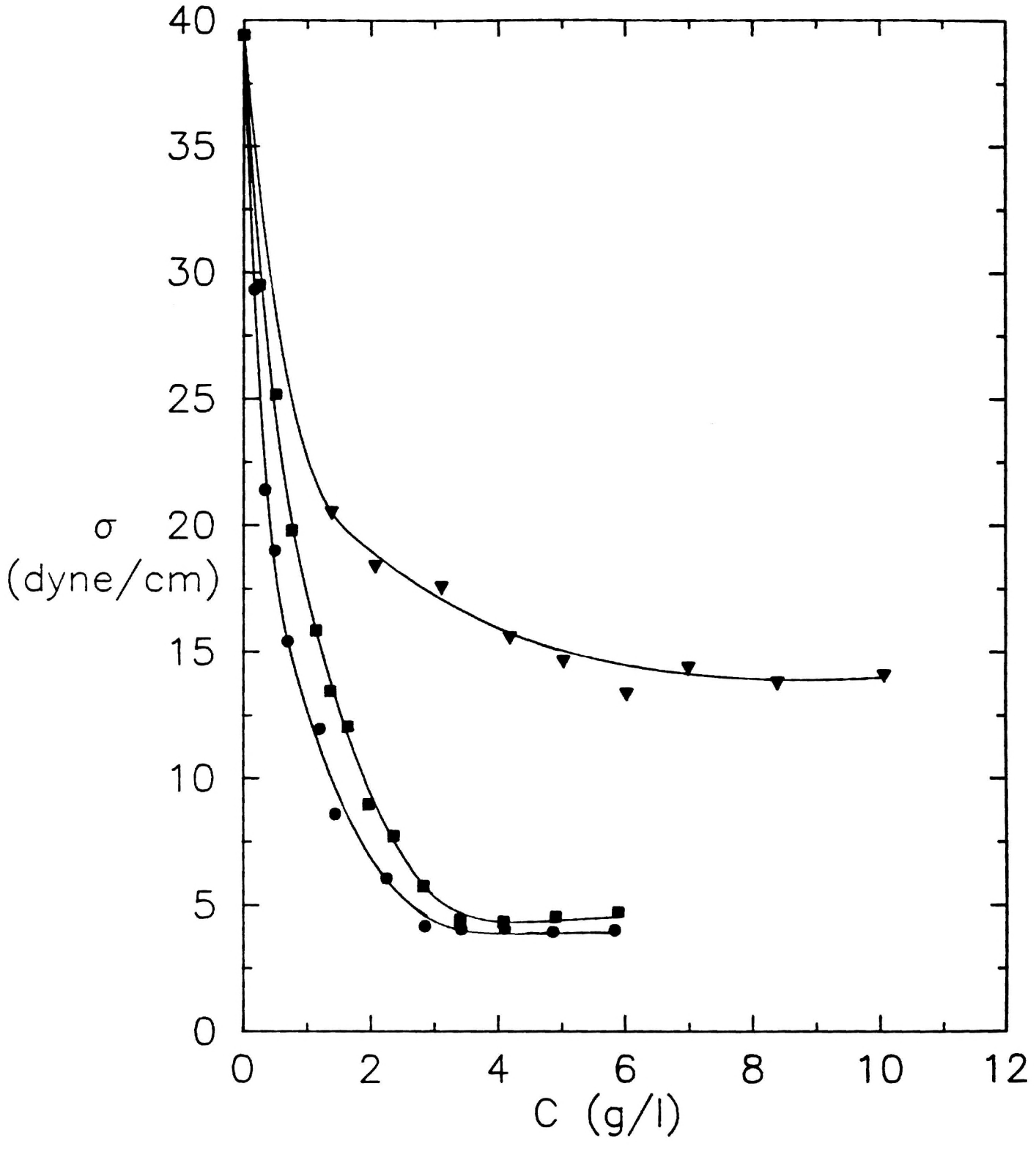

Figure 1 : Diminished value of interfacial tension due to the presence of surfactants (anionic SAA ●, cationic SAA ■, nonionic SAA ▼).

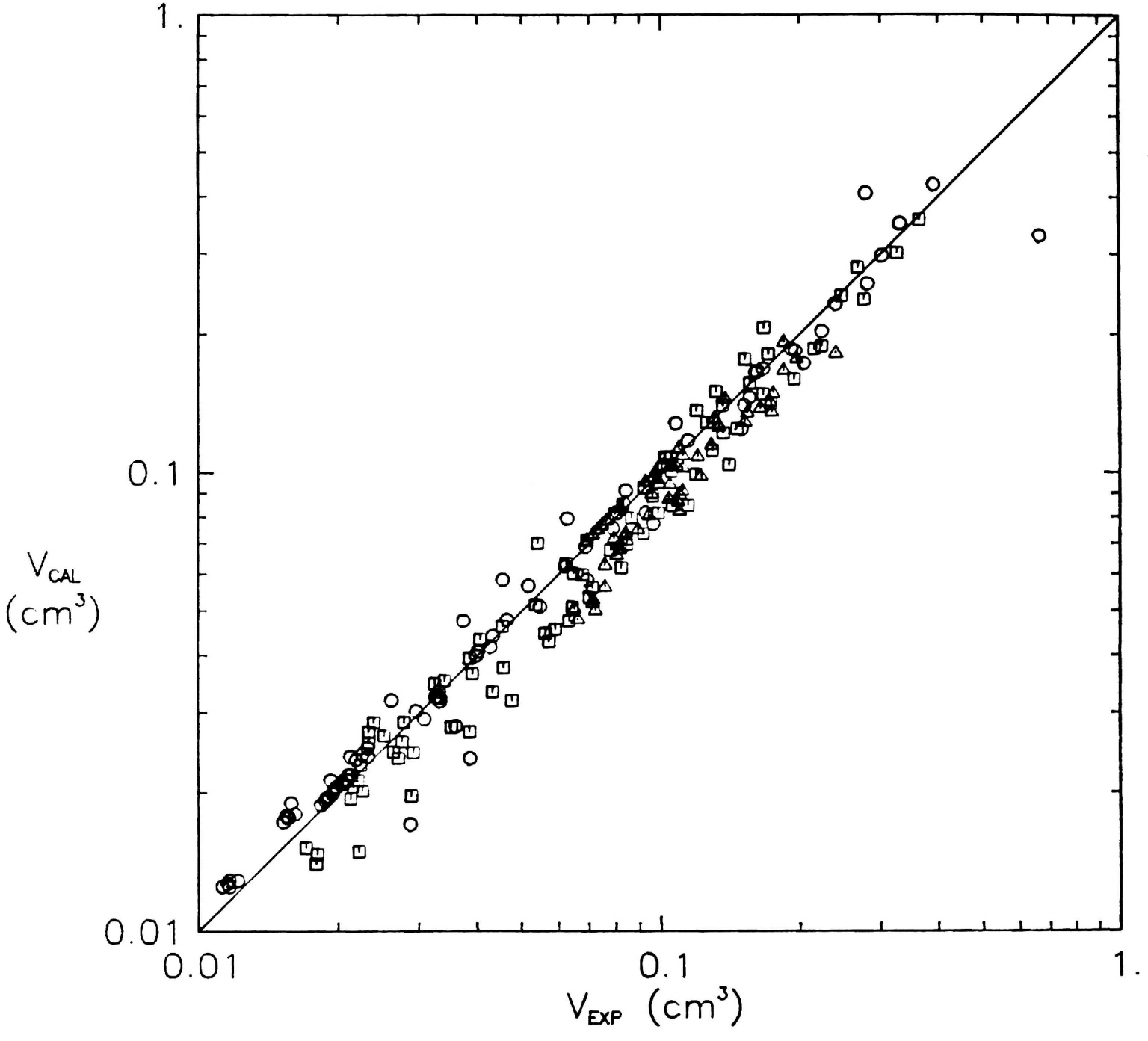

Figure 2 : Comparison between drop volume predicted by the Scheele and Meister equation and experimental data (anionic ○, cationic □, nonionic △).

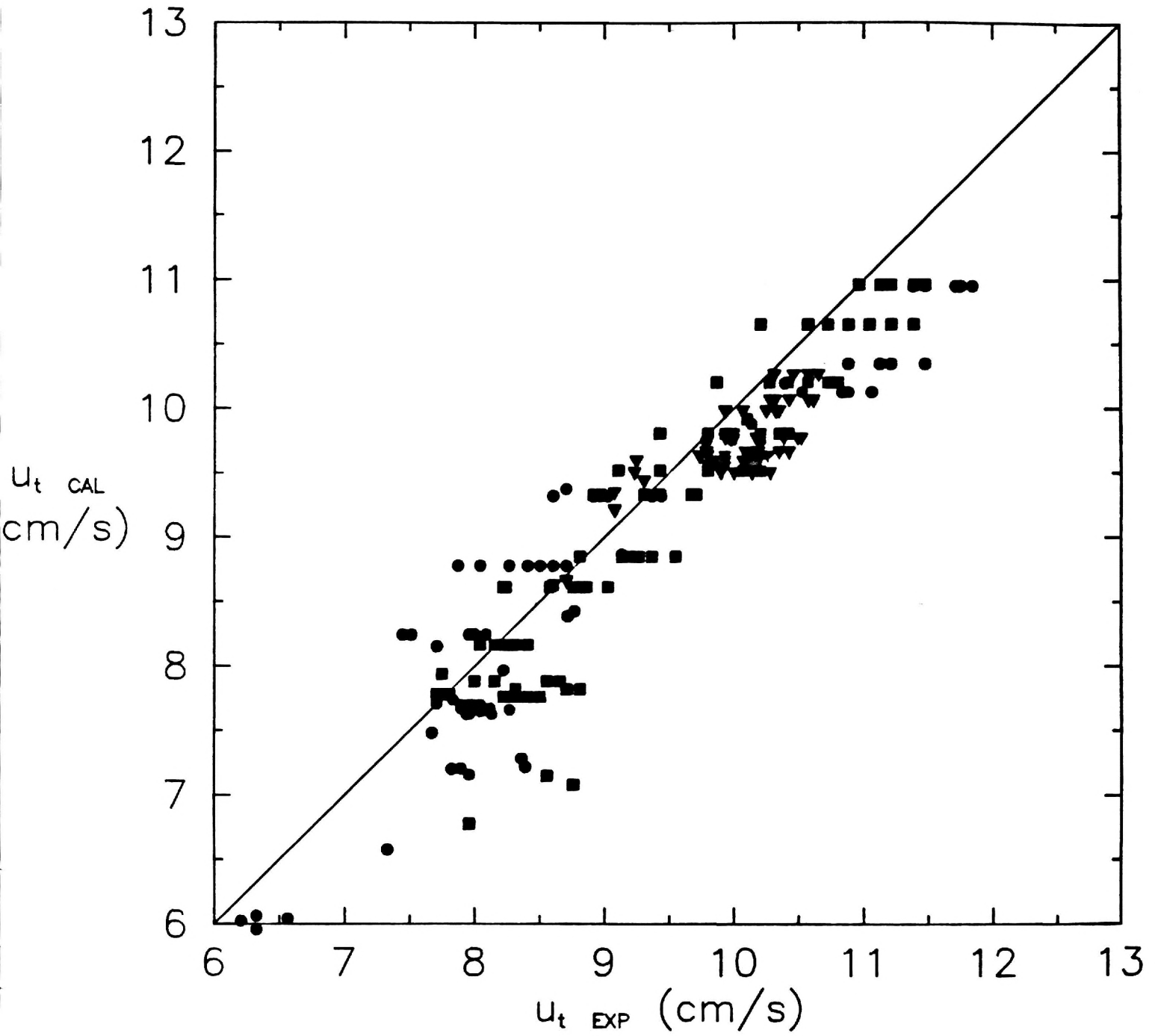

Figure 3 : Comparison between terminal velocities predicted by Klee and Treybal's Correlation 4 (anionic SAA ●, cationic SAA ■, nonionic SAA ▼).

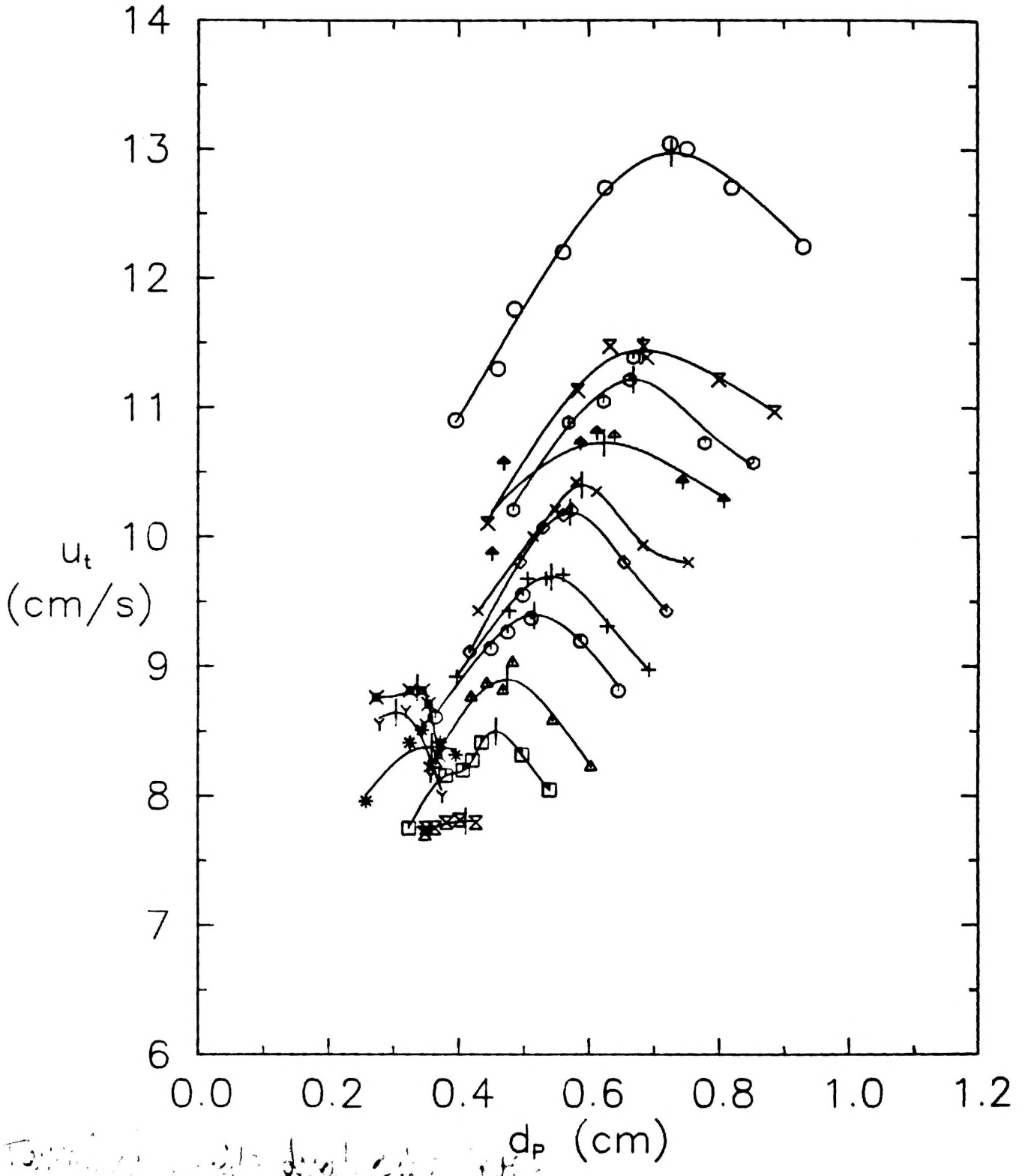

Figure 4 a : Onset of oscillation in the presence of the cationic SAA (symbols given on the next page).

Figure 4a Symbols - Vertical line through symbol indicates onset of oscillation.

Run	Symbol	Concentration (g/ℓ)
1	○	0.00
2	×	0.25
3	⬡	0.51
4	◇	0.76
5	×	1.14
6	◇	1.36
7	+	1.64
8	⬡	1.96
9	△	2.36
10	□	2.83
11	⧖	3.41
12	✳	4.09
13	⌘	4.90
14	Y	5.88

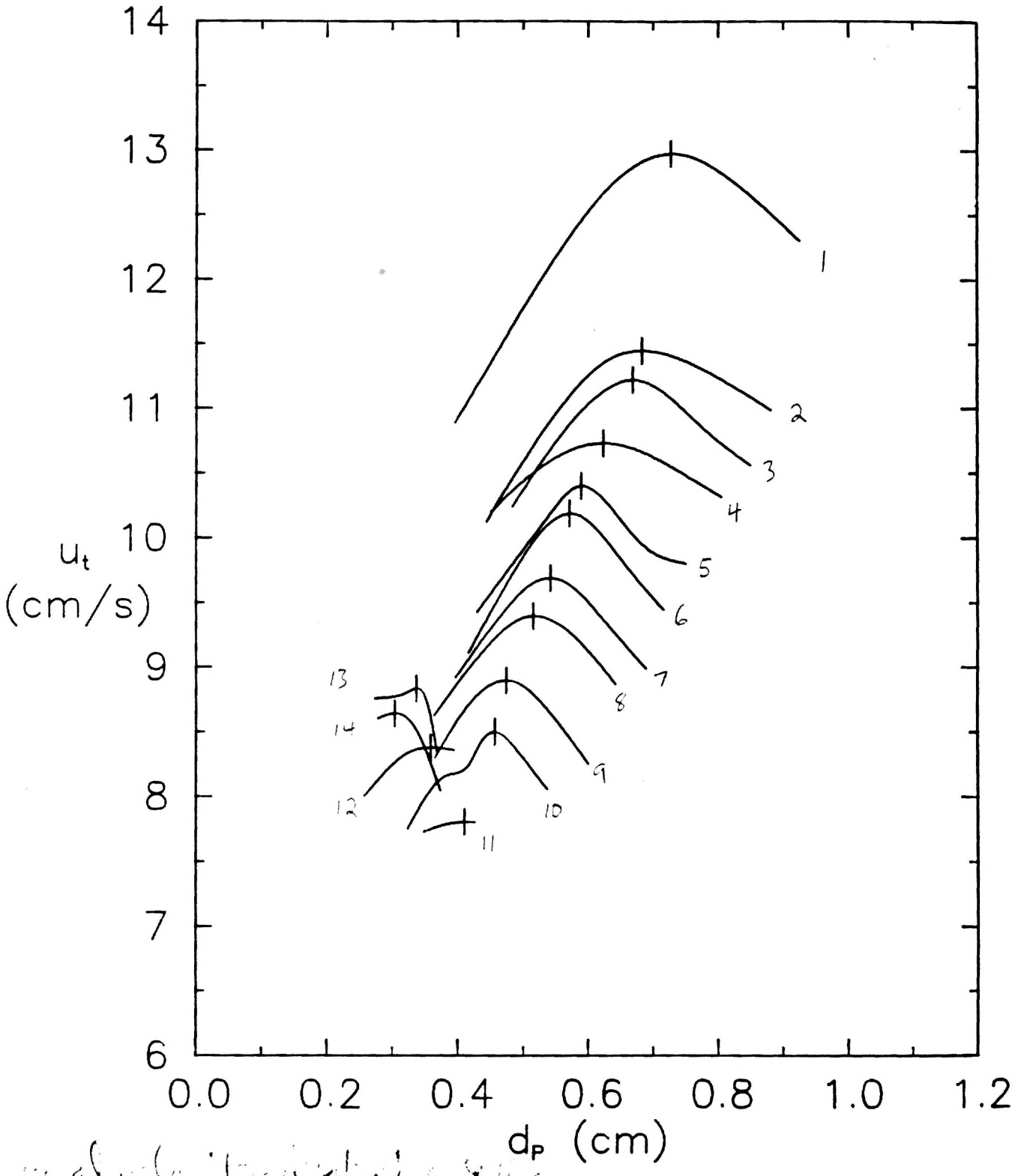

Figure 4 b': Onset of oscillation in the presence of the cationic SAA (vertical line indicates onset of oscillation, numbers represent the run).

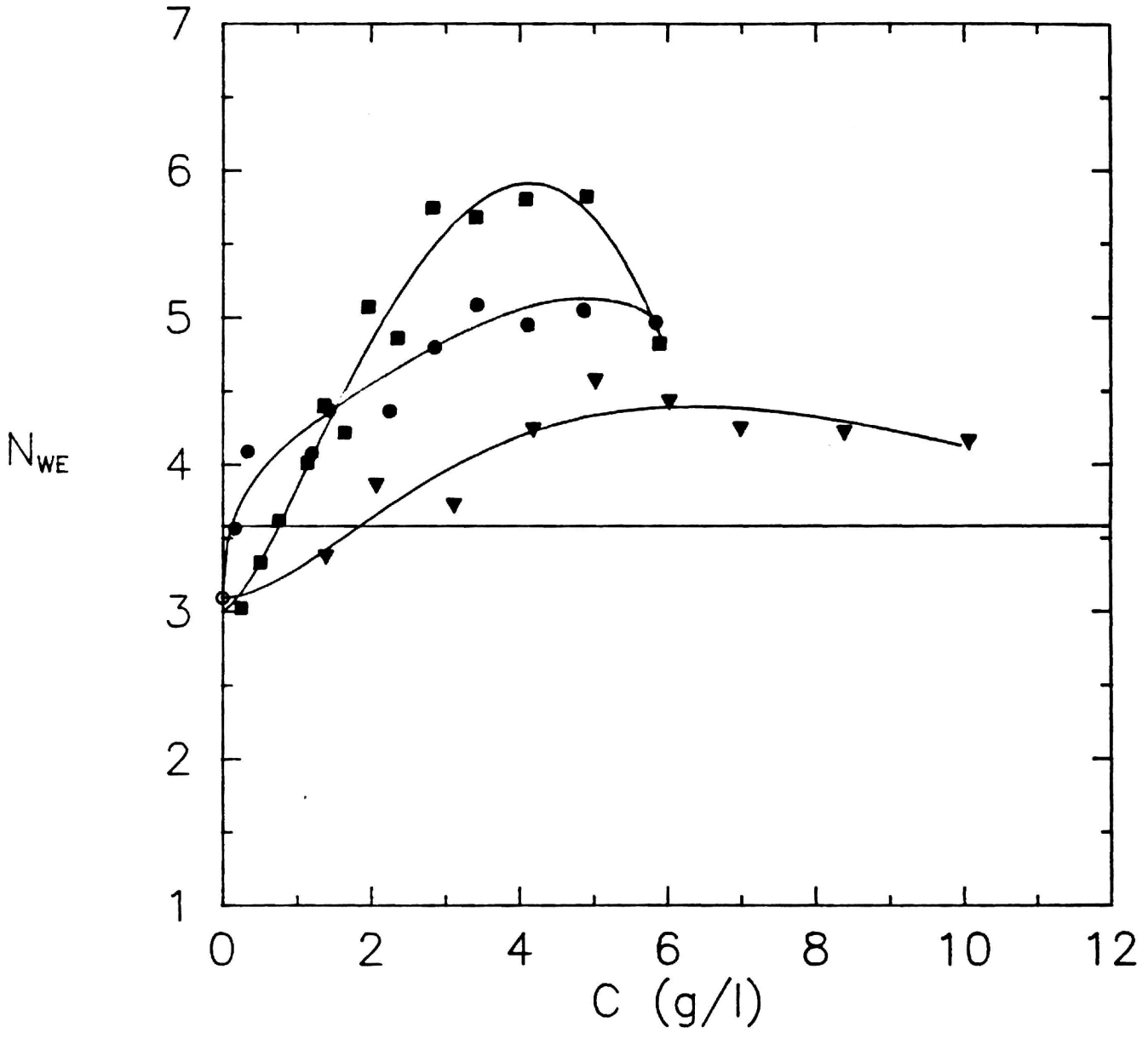

Figure 5 : Weber number at the onset of droplet oscillation (anionic SAA ●, cationic SAA ■, nonionic SAA ▼).

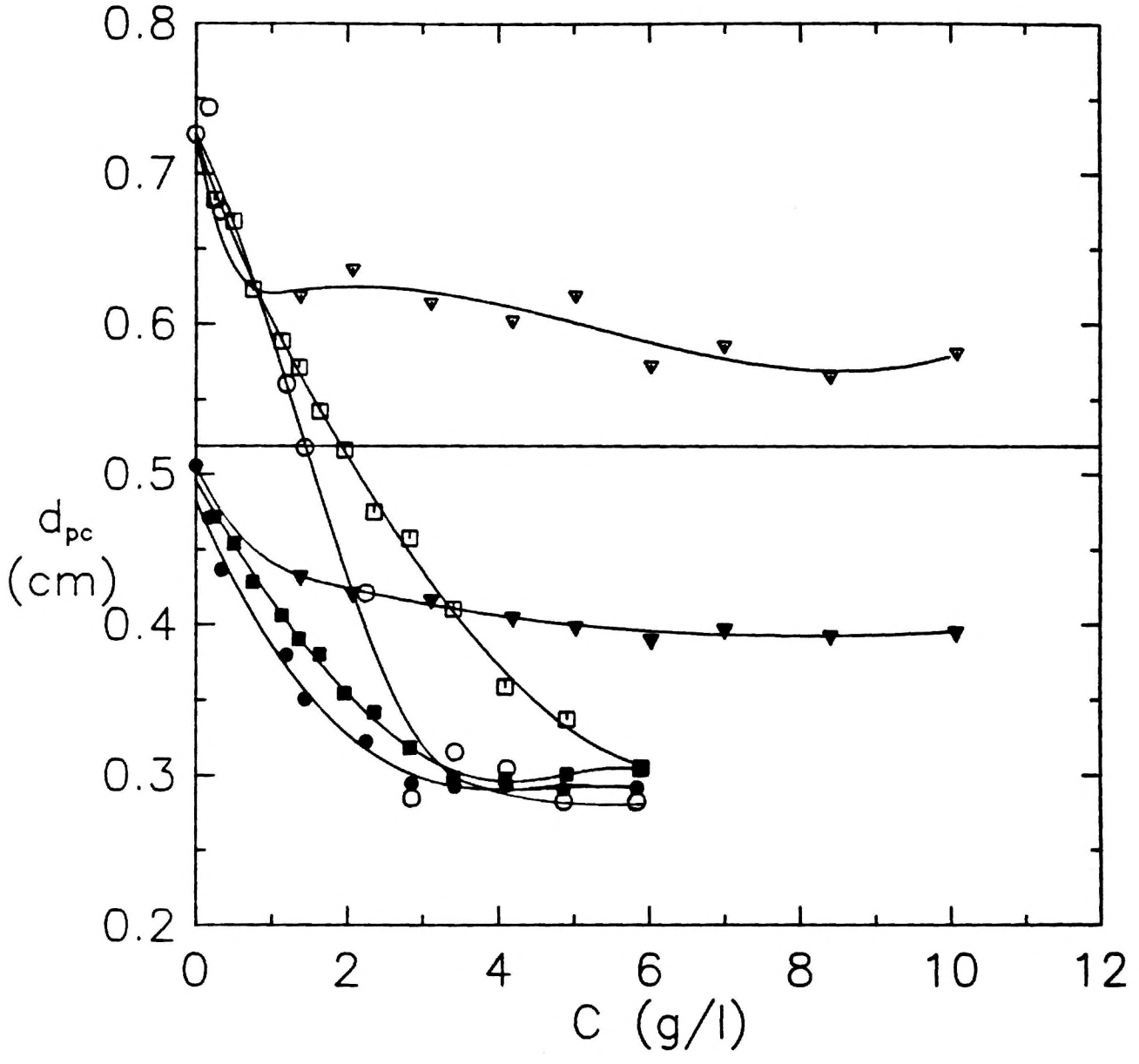

Figure 6 : Drop diameter at onset of oscillation (anionic SAA ○, cationic SAA □, nonionic SAA ▽; corresponding solid symbols represent values predicted by Klee and Treybal; horizontal line at d_{pc} = 0.52 cm represent Edge and Grant's predicted value).

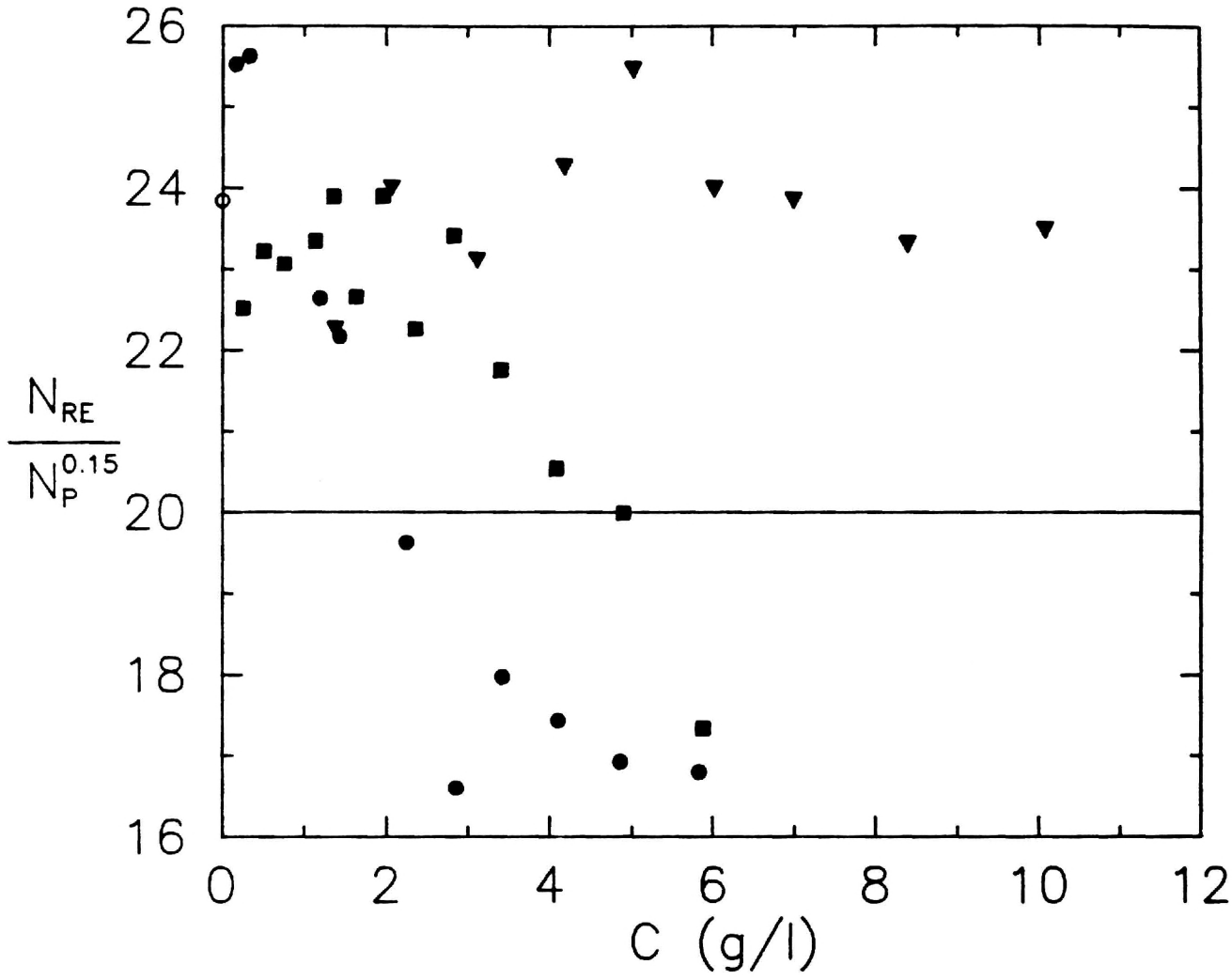

Figure 7 : Johnson and Braida's criterion for onset of droplet oscillation ($N_{Re} / N_P^{0.15} = 20$) compared with experimental data (pure system ○, anionic SAA ●, cationic SAA ■, nonionic SAA ▼)

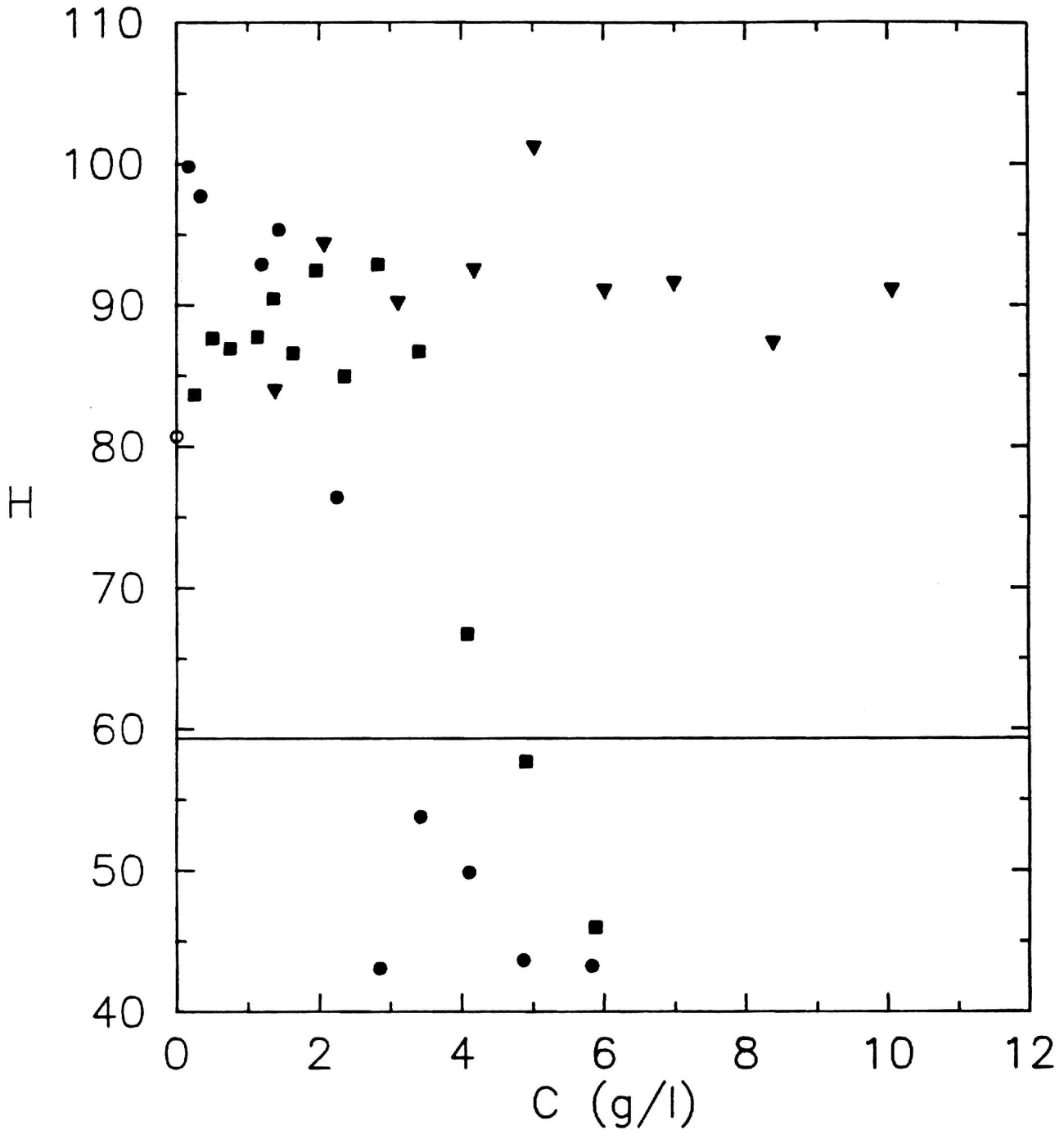

Figure 8 : Grace, Wairegi, and Nguyen's criterion for onset of droplet oscillation ($H = 59.3$) compared with experimental data (pure system ○, anionic SAA ●, cationic SAA ■, nonionic SAA ▼).